

The influences of the mining activities on surface, underground water and river sediments in Crisul Alb catchment

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1. Abstract

In order to establish the level of water pollution with heavy metals and inorganic anions in Crisul Alb River, one of the most important Romanian rivers, total and dissolved metals (Mn, Fe, Cu, Zn, Cd and Pb) sulfates, nitrates and chlorides were determined. The metal concentrations from river sediments were also determined. In order to estimate the underground water contamination, water samples from two domestic wells were analyzed. The determinations of metals and anions were carried out using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Ion Chromatography (IC). The obtained values indicate a slight pollution of the Crisul Alb River and a variable distribution of metals in water and in particulate mater, depending of the type of the metal.

2. Introduction

Crisul Alb River is one of the most important Romanian rivers, coming from Apuseni Carpatian Mountains and joining the Tisza River in Hungary. The Tisza is itself a tributary to the Danube River that flows until the Black Sea. Mining activities in the Apuseni Mountains have left a legacy of large-scale soil and water contamination with metals (Bird et al., 2003). Romania's major deposits of non-ferrous metals contain metals such as copper, zinc, cadmium and lead, together with minerals rich in sulfides. The upper part of Crisul Alb catchments (Brad area) is well known for its base metal resources.

Sulfide mineralization is well known for its potential to produce acid drainage and leaching of contaminants during and after mining exploitations, often resulting in pollution of surface and groundwater (Biddau et al, 2005, Dold et al, 2001).

The aim of this paper was to establish the level of surface and underground water pollution with metals (Cu, Zn, Cd, Pb, Cr, Mn, Fe) and anions (sulfates, nitrates and chlorides) in Crisul Alb River, and the concentrations of metals in sediments along the river.

3. Methods

Sample collection

In July 2006, 14 water samples were collected: 10 samples along the Crisul Alb River (CA1 – CA10) from Brad area to Hungarian border, 2 from tributaries (Valea Arsului, VA1, and Valea Bucuresciului, BU1) and 2 from domestic wells, situated in the vicinity of the river. Also, 10 sediment samples were collected along the Crisul Alb River, from the same sampling points as the river water samples. The sampling points are presented in figure 1.

On each site, three water samples were taken and prepared as follows: i) acidulated by adding of concentrated nitric acid until pH < 2, for total metals determination; ii) filtered and acidulated (pH < 2) for dissolved metals determination and iii) filtered for anions determinations. For filtration, syringes with attachable filter holder were used on the field, with a 0.45 µm pores filter. The sediment samples were collected in paper bags, air dried and sieved. Fraction below 100 µm was stored in polyethylene bags until analysis.

Instrumentation and materials

Analytical grade chemicals and ultrapure water (18 MΩ cm⁻¹, Direct Q UV 3 Millipore system) were used to prepare all solutions.

The metals determinations were carried out using Inductively Coupled Plasma Atomic Emission spectrometer SPECTROFLAME (Spectro Analytical Instruments Kleve, Germany). All relevant ICP spectrometer operating parameters such as r.f. power level, gas flows, sample uptake rate and positioning of the torch in the front of the optical interface were controlled by the software.

An Ion Chromatograph model 761 Compact from Metrohm with chemical suppression, IC Anion Metrosep Supp 5 – 100 column with carbonate eluent (1.0 mmol/L sodium hydrogen carbonate and 3.2 mmol/L sodium carbonate) was used for determination of anions.

OI Analytical Microwave Digestion System with pressure control was used for sediment samples digestion.

The dissolved metals, due to the low concentrations, were determined after a preconcentration using Solid Phase Extraction procedure. The enrichment factor was about 10. The preconcentration was applied using a modified vacuum filtration unit with sorber column (Bakerbond phenyl sorber) and 50 ml polyethylene storage container (Sartorius). In order to avoid samples contamination, sample preparation was made in clean bench (SKAN AG HFX 120).

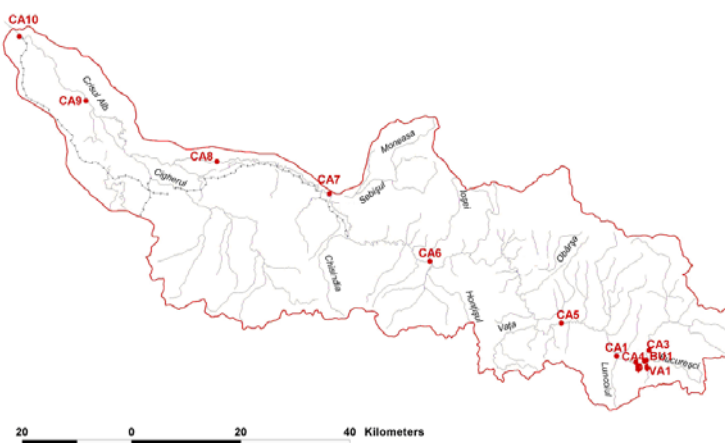
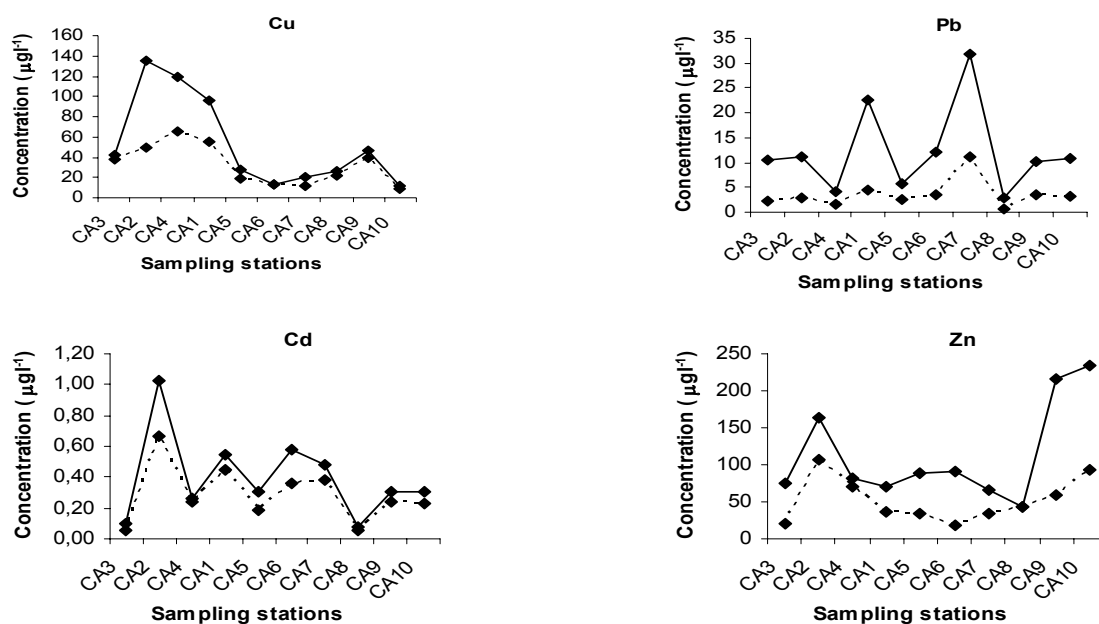


Figure 1 Sampling points in Crisul Alb Catchment

The total metal contents from water were determined after sample digestion in a microwave oven, using acid mixture. The microwave oven was used for metals digestion from sediment samples using acid mixture: $\text{HNO}_3 : \text{HCl}$ (1:3).

4. Results

The variation of total and dissolved metal contents in Crisul Alb River from upstream to downstream is presented in figure 2.



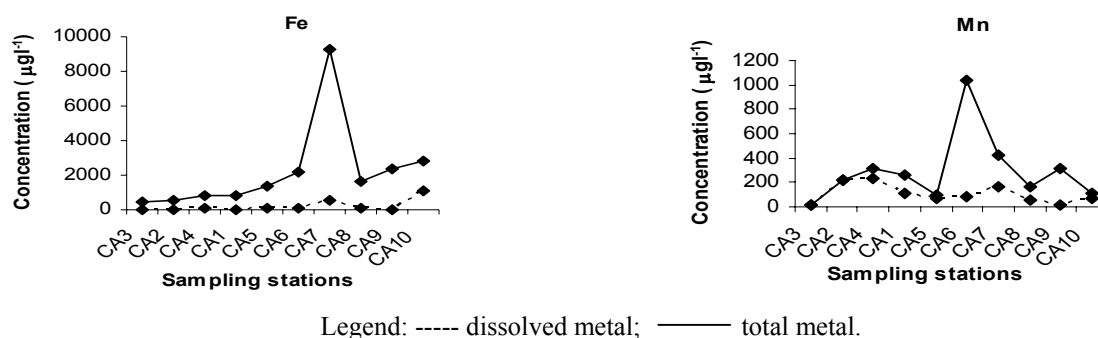


Figure 2 Longitudinal profile of total and dissolved metals in the Crisul Alb River

The metal content of the rivers is a consequence of: geochemistry of the rocks in the catchments area (metals released into the water by weathering); anthropogenic pollution (by waste inputs and atmospheric deposition); river chemistry (adsorption of metals ions to particles and other surfaces and particle deposition into the sediments) (Stumm, 1992).

The influence of geochemistry was determined by analyzing a sampling point unaffected by the anthropogenic activities (as background). The water sample CA3 is considered as background concentration for Crisul Alb catchment, since it is situated upstream from the mining activities.

The results show that a part of metal contents in Crisul Alb is due to the natural background (geochemistry of the rocks). In the sampling points from tributaries (Valea Arsului, VA1, and Valea Bucurestiului, BU1), directly affected by mining activities, high content of metals and low pH values (around 4) were found. The two tributaries change the Cu and Cd concentrations in upper part of Crisul Alb River (Brad area - sampling point C1, C2 and C4), but the increase of concentrations are not drastic due to the small flow-rate of tributaries comparing with that of Crisul Alb. The concentrations of Cu and Cd decrease in the lower part of the river. The concentrations of Zn, Pb, Fe, Mn are generally homogenous along the Crisul Alb river. In the majority of samples from Crisul Alb, the concentrations of Cr were below detection limit (2.1 µg/l).

Comparison between the total and dissolved metals concentration show that the Pb is predominantly in particulate form with an average of 70 – 90%. Also, Fe was found predominantly in particulate form 80 – 90 %, and the percentages of Cd, Zn, Mn and Cu in particulate form were 30 – 50%, 60 – 80%, 40 – 70% and 30 – 60% respectively. These high proportions of particulate metals are characteristic for large rivers that are rather unpolluted and characterized by high turbidity. The values of pH measured were in the range of 6.5 – 7.5 in all water samples from Crisul Alb River.

The concentrations of sulphates ranged between 16 – 69 mg/L. Sulfate contents indicate the impact of mine wastewaters on the rivers, especially in Brad mining area. The concentrations of chlorides (2,6 – 19,2 mg/l) and nitrates (1,23 – 3,43 mg/l) indicate a slight pollution of Crisul Alb catchments due to domestic activities. In tributary BU1, the high content of sulphates (1200 mg/l) indicates an important pollution influenced by the mining activities.

The metal contents in the underground waters (two domestic wells) were, in the most cases below detection limits.

In Romanian legislation (Romanian Order no. 161/2006 – Ministry of waters, forests and environmental protection), 5 quality classes for surface water are indicated, the quality decreasing from class I to class V. Water quality in Crisul Alb river are, according Romanian legislation, in different points, in class III or IV due to the high content of iron. The concentrations of others metals and anions are relatively low, showing a small pollution of the river.

The variation of metal contents in sediments from Crisul Alb River from upstream to downstream is presented in figure 3.

In Romanian legislation maximum admitted limits are established for toxic metals. In case of Cu, the maximum admitted limit is 40 mg/kg. In Brad area, in samples CA1, CA2, CA4, CA5, directly influenced by the mining activities, the maximum admitted level was overreached about 2 times. A decreasing trend is observed along the river, the values of concentration were below maximum admitted limit in the last three sampling points. In case of Pb, the maximum admitted limit is 85 mg/kg and no overreaching was observed. A trend similar with that of Cu (increasing in Brad area) followed of decreasing along the river is observed. Zn has a similar distribution. The maximum admitted limit of 150 mg/kg was overreached in Brad area and was close to this limit before and after this region.

In case of Cd, the maximum admitted limit of 0.8 mg/kg are overreached 2-3 times in all samples. The highest values were also in Brad area, but the distribution along the river was generally homogenous. The high concentrations of Cd might be the result of natural background due to the fact that high concentrations was observed in CA3, considered as background value not affected by mining activities.

In case of Fe and Mn, maximum admitted limits were not regulated. The concentration are homogenous along the river, except for Fe in sampling point CA1 affected by acidic mine water drainage.

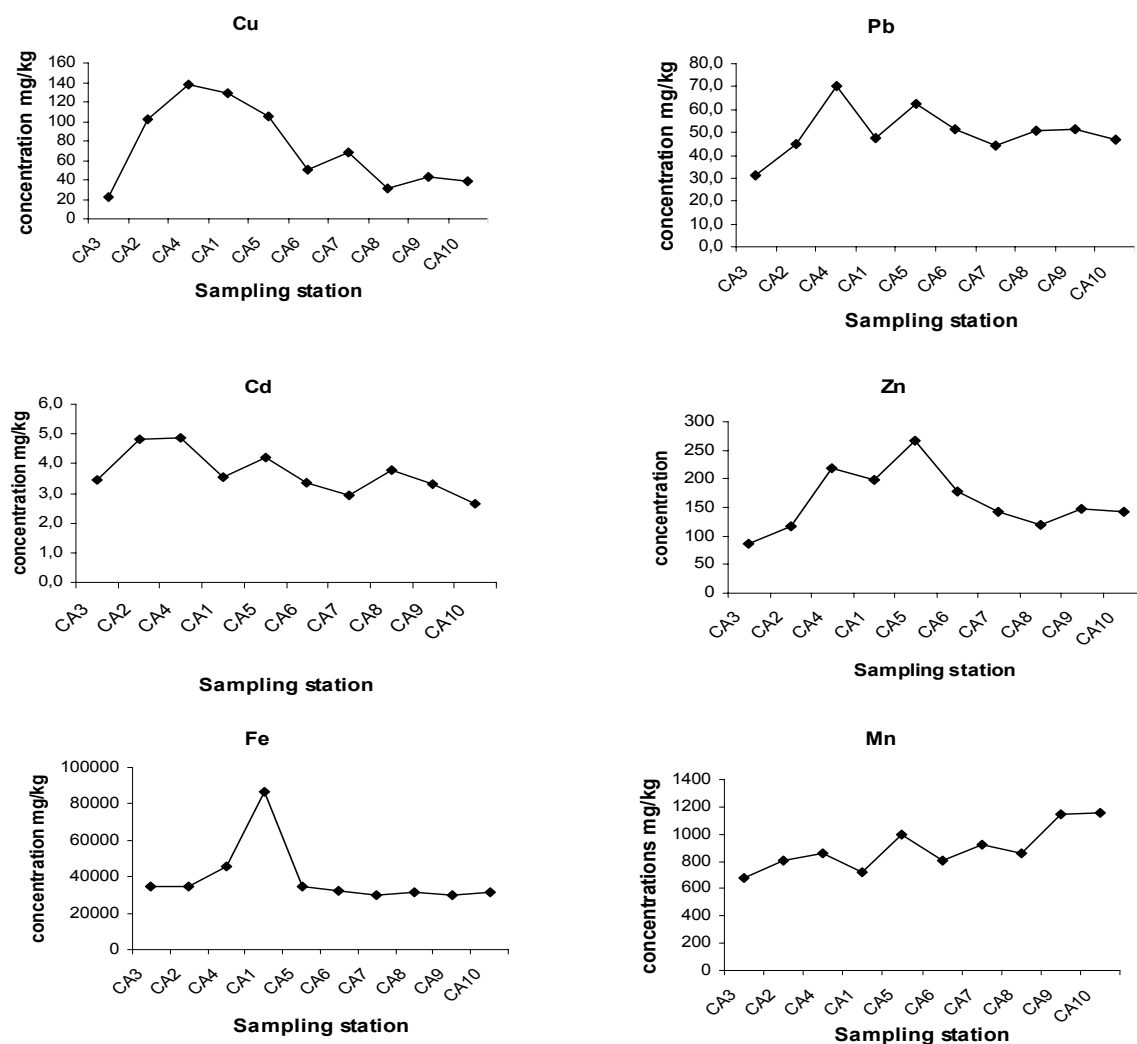


Figure 3 Longitudinal profile of metals in sediments from Crisul Alb River

A contamination of surface water is still possible in the future due to the long term contamination potential of the tailings from Crisul Alb area. The small water flows from Valea Arsului and Valea Bucurestiului, will remain in a critical state due to acidic mine water drainage. For this reason, further investigations and monitoring are necessary.

5. Acknowledgements

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6. References

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